ORIGINAL ARTICLE

Structure and Biological Behaviors of Some Metallo Cationic Surfactants

Ahmed I. Adawy · Mnal M. Khowdiary

Received: 23 October 2012/Accepted: 10 April 2013/Published online: 27 April 2013 © AOCS 2013

Abstract In this study, different cationic surfactants were prepared by esterification with bromoacetic acid of different fatty alcohols, i.e., dodecyl, tetradecyl and hexadecyl species. The products were then reacted with diphenyl amine, and the resulting tertiary amines were quaternized with benzyl chloride to produce a series of quaternary ammonium salts. The metallocationic surfactants were prepared by complexing the cationic surfactants with nickel and copper chlorides. Surface tension of these surfactants were investigated at different temperatures. The surface parameters including critical micelle concentration (CMC), maximum surface excess (Γ_{max}), minimum surface area (A_{\min}), efficiency (PC₂₀) and effectiveness (π_{CMC}) were studied. The thermodynamic parameters such as the free energy of micellization $(\Delta G_{\rm mic}^{\circ})$ and adsorption (ΔG_{ads}°) , enthalpy (ΔH_{m}°) , (ΔH_{ads}°) and entropy (ΔS_{m}°) , (ΔS_{ads}) were calculated. FTIR spectra and ¹H-NMR spectra were obtained to confirm the compound structures and purity. In addition, the antimicrobial activities were determined via the inhibition zone diameter of the prepared compounds, which were measured against six strains of a representative group of microorganisms. The results indicate that these metallocationic surfactants exhibit good surface properties and good biological activity on a broad spectrum of microorganisms.

Electronic supplementary material The online version of this article (doi:10.1007/s11743-013-1483-z) contains supplementary material, which is available to authorized users.

A. I. Adawy (⊠) · M. M. Khowdiary Petrochemicals Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt e-mail: chem_ahmedadawy@yahoo.ca **Keywords** Cationic surfactants · Surface parameters · Biological activity

Introduction

Cationic surfactants offer some additional advantages over other classes of surfactants [1–4]. Besides their surface activity, these substances show antibacterial properties and are used as cationic softeners, lubricants, retarding agents and antistatic agents.

Quaternary salt species are well known compounds and have been examined for their surface and solution behavior using a variety of methods [5–14].

Micelle formation of a surfactant in solution is induced by the hydrophobic interaction between hydrocarbon parts of the surfactant molecules balanced by their hydration and electrostatic repulsive effects [15].

The metal–surfactant complex is a special type of surfactant, where a coordination complex (containing a central metal ion with surrounding ligands coordinated to the metal) acts as the surfactant (Scheme 1).

In these surfactants, the metal complex entity containing the central metal ion with its primary coordination sphere, acts as the head group and the hydrophobic entity of one or more ligands acts as the tail part. Surfactant metal complexes are expected to provide a wide range of interesting phenomena on aggregation in aqueous solution due to variations in charge numbers, size and extent of hydrophobicity through combination of the central metal and ligands [16]. The biological active compounds generally become more bacteriostatic and carcinostatic upon chelation with metal ions [17].

The aim of this paper was to prepare some of metallocationic surfactants and determine their surface and thermodynamic properties and evaluate them as biocides. Scheme 1 Preparation of metallocationic surfactants n = 10 (I:Id), 12 (II:IId), and 14 (III:IIId)



Id, IId and IIId

Ic, IIc and IIIc

Experimental Procedures

Materials

The chemicals used in this study were of pure grade from Aldrich and were used without further purification. The solvents used were of pure grade too.

Synthesis

- 1. As shown in Scheme (1), the syntheses of compounds (I, II and III) were carried out by refluxing different fatty alcohols, i.e., dodecyl, tetradecyl and hexadecyl alcohol (1 mol) with bromoacetic acid (1 mol) in a Dien Shtark system in xylene.
- 2. The syntheses of compounds (Ia, IIa and IIIa) were realized by refluxing ester compounds (I, II and III) (1 mol) with diphenyl amine (1 mol) for 6 h in benzene. The reaction mixtures were left to cool then filtered.

- 3. The quaternary ammonium compounds (Ib, IIb and IIIb) were synthesized by refluxing tertiary amines (Ia, IIa and IIIa) (1 mol) with benzyl chloride (1 mol) for 90 h in benzene. The solid product was filtered and recrystallized from benzene to obtain the cationic surfactant named alkyl acetate benzyl diphenyl ammonium salt.
- 4. Syntheses of metal complexes (metallosurfactants) were carried out by refluxing 2 mol of cationic surfactants Ib, IIb and IIIb once with 1 mol of nickel chloride (NiCl₂) in benzene for 4 h to obtain metal complexes Ic, IIc and IIIc, respectively. The same was repeated with 1 mol of copper chloride (CuCl₂·2H₂O) in benzene for 4 h to obtain metal complexes Id, IId and IIId. The reaction mixtures were left to cool then filtered.

Structural Confirmations of the Prepared Compounds

The chemical structure of the synthesized compounds was characterized by the following analysis.

Depringer ACCS *

The FTIR spectra were obtained using ATI Mattsonm Infinity seriesTM, Bench top 961 controlled by Win FirstTM V2.01 software. (Egyptian Petroleum Research Institute). On the other hand ¹H-NMR was measured in DMSO-d₆ by Spect Varian, GEMINI 200 (¹H 200 MHz). (Micro Analytical Center, National Research Center).

Evaluation Methods of Surface Active Properties

Surface Tension

Surface tensions of the prepared compounds solutions were measured using a Du-Nouy Tensiometer (Krüss type 6). The surface tensions of different concentrations over a range of 4×10^{-2} to 1.9×10^{-5} mol/l at different temperatures (35, 45, 55 and 65 °C) were measured.

Surface Parameters of the Prepared Compounds

Critical Micelle Concentration (CMC) The values of the critical micelle concentration of the prepared compounds were determined using the surface tension technique. The surface tension measurements were plotted against the corresponding concentration in a log scale, and the break point was taken as the CMC.

Effectiveness (π_{CMC}) π_{CMC} is the difference between the surface tension of the pure water (γ_o) and the surface tension of the surfactant solution (γ) at the critical micelle concentration.

$\pi_{\rm CMC} = \gamma_{\rm o} - \gamma_{\rm CMC}$

Efficiency (PC_{20}) Efficiency (PC_{20}) is determined as the concentration (mol/l) of the surfactant solutions capable to reduce the surface tension by 20 mN/m.

Maximum Surface Excess $\Gamma_{\rm max}$ The values of the maximum surface excess $\Gamma_{\rm max}$ calculated from surface or interfacial data by the use of Gibbs equation [18].

 $\Gamma_{\max} = -1/2.303 nRT \left(\frac{\partial \gamma}{\partial \log C}\right)_T$

where Γ_{max} is the maximum surface excess in mol/cm², *n* is the number of solute species whose concentration at the interface changes with change in the value of *C* and equal to 2 for conventional ionic surfactants, *R* the universal gas constant 8.31×10^7 ergs mol⁻¹ K⁻¹, *T* the absolute temperature (273.2 °C), *C* the surfactant concentration, $(\partial \gamma / \partial \log C)_T$ the slope of the plot surface tension vs. $-\log C$ curve just below CMC at constant temperature.

Minimum Surface Area (A_{\min}) The area per molecule at the interface provides information on the degree of packing and the orientation of the adsorbed surfactant molecule. The average area (in square angstrom) occupied by each molecule adsorbed on the interface [19] is given by:

$$A_{\min} = 10^{16} / \Gamma_{\max} N_{\mathrm{A}}$$

where $N_{\rm A}$ is the Avogadro's number 6.023 $\times 10^{23}$;

Thermodynamic Parameters of Micellization and Adsorption The thermodynamic parameters of adsorption and micellization of the synthesized cationic surfactants were calculated according to Gibb's adsorption equations as follows [20]:

$$\Delta G_{\text{mic}}^{\circ} = RT \ln(\text{CMC})$$

$$\Delta G_{\text{ads}}^{\circ} = \Delta G_{\text{mic}}^{\circ} - 6.023 \times 10^{-1} \times \pi_{\text{CMC}} \times A_{\text{min}}$$

$$\Delta S_{\text{mic}} = -d \left(\Delta G_{\text{mic}}^{\circ} / \Delta T \right)$$

$$\Delta S_{\text{ads}} = -d \left(\Delta G_{\text{ads}}^{\circ} / \Delta T \right)$$

$$\Delta H_{\text{mic}} = \Delta G_{\text{mic}}^{\circ} + T \Delta S_{\text{mic}}$$

$$\Delta H_{\text{ads}} = \Delta G_{\text{ads}}^{\circ} + T \Delta S_{\text{ads}}$$

Antimicrobial Activity of the Prepared Compounds

The antimicrobial activities of the prepared metallocationic surfactants were measured individually against a wide range of microorganisms previously isolated in the Biotechnology Lab. in the Egyptian Petroleum Research Institute (EPRI) from different oil polluted environments using a dose equal to 5 mg/ml by the diffusion agar technique.

The microorganisms included gram-positive bacteria (*Bacillus pumilus* and *Micrococcus luteus*), gram-negative bacteria (*Pseudomonas aeruginosa* and *Sarcina lutea*), yeast (*Candida albicans*) and fungi (*Penicillium chrysogenum*).

Results and Discussion

Chemical Structure

The chemical structure of the prepared cationic surfactants was confirmed by FTIR and ¹H-NMR spectra.

FTIR Spectra

The FTIR spectra of the synthesized compounds showed the following absorption bands at 1,732.75–1,740.8 cm⁻¹ for the C=O ester group, 2,853–2,857.25 cm⁻¹ for the CH₂ group and 2,925.87–2,918.97 cm⁻¹ for the N⁺ group, see Figs. (S1–S6) in the supplementary material. The FTIR spectra confirmed the expected functional groups in the synthesized cationic surfactants.

¹H-NMR Spectra

¹H-NMR spectra of synthesized complexes showed signals at: $\delta = 0.89$ ppm (t, 3H, CH₃), 1.39 ppm (s, 2H, CH₂),

1.29 ppm (q, nH, CH₂), 4.13 ppm (t, 2H, CH₂), 4.21 ppm (s, 2H, CH₂), 4.4 ppm (s, 2H, CH₂) and 7.25 ppm (d, 1H, CH phenyl), where n = 18, 22 or 26 for complexes Id, IId and IIId, respectively, see Figs. (S7–S12) in the supplementary material. The data of the ¹H-NMR spectra confirmed the expected hydrogen proton distribution in the synthesized complexes. All the synthesized complexes had approximately the same values.

Surface Properties

Surface Tension

The surface tension was measured for aqueous solutions of the prepared metallocationic surfactant with different concentrations (4 × 0.01 to 1.9×10^{-5} mol/l) and at different temperatures (35, 45, 55 and 65 °C). The data are represented in surface tension-concentration curves as shown in Figs. 1, 2, 3, 4. It is clear that surface tension decreases by increasing the concentration of the metallocationic complexes, due to increasing the migration of the surfactant molecules from the bulk to the interface of the solution. The figures also show that the surface tension values decrease as the temperature increase from 35 to 65 °C.

It was expected that the surface tension values of the cationic complexes (Ic, Id, IIc, IId, IIIc and IIId) would be lower than for the parent cationic surfactants (Ib, IIb and IIIb). This is the result of the increase in the hydrophobicity of these complexes in comparison to the parent cationics, which is due to the presence of two ligands coordinated to the metal ion [21], i.e., an increase in the non polar part. Consequently, the water/surfactant molecules' interactions decrease, which force them to the air–water interface [22] with a surface tension decrease.

The Critical Micelle Concentration (CMC)

Critical micelle concentration values of the prepared metallocationic surfactants were determined by plotting the



Fig. 1 Surface tension versus log Concentration of complexes at 35 $^{\circ}\mathrm{C}$

surface tension (γ) of surfactant solutions versus their bulk concentrations in mol/l in a log scale at 35, 45, 55 and 65 °C. The CMC values are listed in Tables 1, 2, 3, and 4 showing a decrease in the CMC with increasing alkyl chain length.

The CMC also decreases as the temperature increases probably due to a decrease in the hydration of the hydrophilic group, which favors micellization. On the other hand, the rise in temperature causes disruption of the



Fig. 2 Surface tension versus log Concentration of complexes at 45 $^{\circ}\mathrm{C}$



Fig. 3 Surface tension versus log Concentration of complexes at 55 $^{\circ}\mathrm{C}$



Fig. 4 Surface tension versus log Concentration of complexes at 65 $^{\circ}\mathrm{C}$

Table 1Surface properties ofthe synthesized metallocationicsurfactants at 35 °C

Surfactant	$CMC \times 10^{-3},$ mol/l	π _{CMC} , mN/m	$\frac{\text{Pc20} \times 10^{-4}}{\text{mol/l}},$	$\Gamma_{\rm max} \times 10^{-11},$ mol/cm ²	A_{\min} , nm ²	
Ic	1.59	22	13	3.3	5	
Id	1.66	23.3	11.5	3.14	5.3	
IIc	1.4	24.2	7.5	3.25	5.1	
IId	1.41	25.6	11	3.7	4.5	
IIIc	1.1	31.27	2.1	3.55	4.7	
IIId	1	30.27	1.3	2.83	5.9	

Table 2Surface properties ofthe synthesized metallocationicsurfactants at $45 \ ^{\circ}C$

Surfactant	$\frac{\text{CMC} \times 10^{-3}}{\text{mol/l}},$	π _{CMC} , mN/m	$\frac{\text{Pc20} \times 10^{-4}}{\text{mol/l}},$	$\Gamma_{\rm max} \times 10^{-11},$ mol/cm ²	A_{\min} , nm ²
Ic	1.46	26.7	11.7	4.4	3.8
Id	1.53	25.12	6.2	3.94	4.2
IIc	1.25	26.25	4.2	3.67	4.5
IId	1.1	26.3	4.9	3.57	4.6
IIIc	0.81	33.5	1.4	3.78	4.3
IIId	0.72	32.6	0.9	2.74	6.1

Table 3 Surface properties of
the synthesized metallocationic
surfactants at 55 °C

Surfactant	$CMC \times 10^{-3},$ mol/l	π _{CMC} , mN/m	$\frac{\text{Pc20} \times 10^{-4}}{\text{mol/l}},$	$\Gamma_{\rm max} \times 10^{-11},$ mol/cm ²	A_{\min} , nm ²	
Ic	1.32	27.74	10	4.1	4	
Id	1.4	27	4	3.82	4.3	
IIc	0.73	28.47	1.9	3.98	4.2	
IId	0.79	28.05	3.6	3.74	4.4	
IIIc	0.52	34.1	0.8	3.47	4.8	
IIId	0.5	32	0.3	2.65	6.2	

Table 4	Surface properties of
the synth	esized metallocationic
surfactan	ts at 65 °C

Surfactant	$\frac{\text{CMC} \times 10^{-3}}{\text{mol/l}},$	π _{CMC} , mN/m	$\frac{\text{Pc20} \times 10^{-4}}{\text{mol/l}},$	$\Gamma_{\rm max} \times 10^{-11}$, mol/cm ²	A_{\min} , nm ²	
Ic	1	28.35	2.9	4	4.1	
Id	1.1	27.85	2.2	4	4.1	
IIc	0.63	30.14	1.4	4.37	3.8	
IId	0.67	29.56	1	4.12	4	
IIIc	0.32	33.67	0.4	3.67	4.5	
IIId	0.33	32.9	0.1	2.57	6.4	

structured water surrounding the hydrophobic group, an effect that disfavors micellization. The relative magnitude of these two opposing effects, determines whether the CMC increases or decreases over a particular temperature range. Data in the Tables 1, 2, 3, and 4 reveal that in this case the CMC decreases upon rising the temperature, i.e., the micellization is enhanced.

Effectiveness (Π_{CMC})

The most efficient surfactant is one that attains the lowest surface tension at the critical micelle concentration (CMC).

According to the results shown in Tables 1, 2, 3, and 4 increasing the alkyl chain length and the temperature improves the effectiveness of the complexes due to an

 Table 5
 The results of the antimicrobial activity of the metallocationic surfactants against tested microorganisms at 5 mg/ml

Tested compounds microorganisms	Ic	Id	IIc	IId	IIIc	IIId
Pseudomonas aeruginosa (Gram –ve)	-ve	13	-ve	-ve	12	17
Sarcina lutea (Gram -ve)	12	-ve	-ve	12	-ve	19
Bacillus pumilus (Gram +ve)	13	12	-ve	-ve	14	18
Micrococcus luteus (Gram +ve)	-ve	-ve	14	-ve	12	22
Candida albicans (Yeast)	-ve	13	-ve	14	13	16
Penicillium chrysogenum (Fungus)	-ve	-ve	12	-ve	-ve	19

increase in the hydrophobicity. Complexes (IIIc and IIId) were found to be the most effective ones at 35 °C, i.e., with a tension of 31.27 and 30.27 mN/m, respectively. They are also the most effective at the other temperatures as seen in Tables 1, 2, 3, and 4.

Efficiency (Pc₂₀)

Efficiency values of the prepared cationic surfactants are given in Tables 1, 2, 3, and 4. From these data it was observed that the efficiency decreases when the length of the alkyl chain and the temperature increase, probably due to the fast formation of monolayer of surfactant at the surface.

Maximum Surface Excess (Γ_{max})

The values of Γ_{max} are reported in Tables 1, 2, 3, and 4). In general the maximum surface excess Γ_{max} rises by increasing the carbon chain length.

Minimum surface area (A_{min})

The minimum area per molecule at the water/air interface for the prepared surfactants is listed in 1, 2, 3, and 4. The minimum surface area (A_{min}) decreases with an increase in the chain length of the hydrophobic part in the surfactant molecule.

Standard Free Energies of Micellization And Adsorption $(\Delta G_{mic}^{\circ}, \Delta G_{ads}^{\circ})$

As shown in Tables (S1–S8) in the supplementary material, the values of $\Delta G_{\rm mic}$ and $\Delta G_{\rm ads}$ are always negative, indicating that these two processes are spontaneous; however, there is a greater increase in the negative value of ΔG_{ads} compared to those of micellization. This suggests a strong tendency of the molecules to be adsorbed at the interface.

Antimicrobial Activity of the Prepared Compounds

The cell membrane of microorganisms is composed of several lipid and protein layers arranged together in specific arrangement called the bilayer (or multilayer lipoprotein structure).

The presence of the lipids as a building unit in the cell membrane gives them their hydrophobic character [23].

The hydrophobic chain length has a remarkable influence on the biological activity on the tested compounds. In general, increasing the hydrophobic chain length increases the biological activity of the surfactants.

The action mode of such metallocationic biocides (Ic, Id, IIc, IId, IIIc and IIId) on the bacterial strains is explained as an electrostatic interaction and a physical disruption. The electrostatic interaction occurs between the oppositely charged centers on the cellular membrane and the positively charged head group of the biocide molecules. On the other hand, the physical disruption is the result from the penetration of the hydrophobic chains into the cellular membrane due to their similarity in chemical nature and structure.

The interaction between the biocide molecules and the cellular membrane causes a strong damage in the selective permeability of these membranes which disturbs the metabolic pathway within the cytoplasm.

As shown in Table 5, the synthesized metallocationic surfactants have moderate activity towards different microorganisms, except compound IIId which exhibits a strong activity, probably because it has the longest alkyl chain length; moreover, it contains a copper ion which has a higher biological activity than the nickel ion. This is certainly due to a lower electronegativity and a larger volume of the copper ion, which increases its molecular area, hence the effective area of the complex on the cell membrane will increase too [24].

References

- 1. Jungerman E (ed) (1969) Cationic surfactants. Marcel Dekker, New York
- Cross J, Singer EJ (1994) Biological evaluation. In: Cross J, Singer EJ (eds) Cationic surfactants: analytical and biological evaluation. Marcel Dekker, New York
- 3. Holland PM, Rubingh DN (eds) (1991) Cationic surfactants: physical chemistry. Marcel Dekker, New York
- Richmond JM (ed) (1990) Cationic surfactants: organic chemistry. Marcel Dekker, New York

- Adamczyk Z, Para G, Warszynski P (1999) Influence of ionic strength on surface tension of cetyltrimethyl ammonium bromide. Langmuir 15:8383–8387
- Bakshi MS (2000) Influence of alkoxyethanols on the mixed micelle formation by hexadecyltrimethyl ammonium bromide and tetradecyl trimethyl ammonium bromide surfactant mixtures. J Colloid Polym Sci 278:1155–1163
- Skerjanc J, Kogej K, Cerar J (1999) Equilibrium and transport properties of alkylpyridinium bromides. Langmuir 15:5023–5028
- Ruso JM, Sarmiento F (2000) The interaction between *N*-alky trimethyl ammonium bromides with poly (L-aspartate): a thermodynamics study. J Colloid Polym Sci 278:800–804
- Zielinski R (2001) Effect of temperature on micelle formation in aqueous NaBr solutions on octyl trimethyl ammonium bromide. J Colloid Interface Sci 235:201–209
- Ranganathan R, Okano LT, Yihwa C, Quina FH (1999) Growth of cetyltrimethyl ammonium chloride and acetate micelles with counter ion concentration. J Colloid Interface Sci 214:238–242
- Fujio K, Mitsui T, Kurumizawa H, Tanaka Y, Uzu Y (2004) Solubilization of water insoluble dye in aqueous NaBr solutions of alkyl pyridinium bromides and its relation to micellar size and shape. J Colloid Polym Sci 282:223–229
- Galan JJ, Gonzalez-Perez A, Del Castillo JL, Rodriguez JR (2002) Thermal parameters associated to micellization of dodecyl pyridinium bromide and chloride in aqueous solution. J Therm Anal Calcd 70:229–234
- Pal OR, Gaikar VG, Joshi JV, Goyal PS, Aswal VK (2002) Small angle neutron scattering studies of mixed cetyl trimethyl ammonium bromide-butyl benzene sulfonate solutions. Langmuir 18:6764–6768
- Ruso JM, Attwood D, Taboada P, Mosquera V (2002) Self association of *N*-hexyltrimethyl ammonium bromide in aqueous electrolyte solution. J Colloid Polym Sci 280:336–341
- 15. Tanford C (1980) The hydrophobic effect-formation of micelles and biological membranes, 2nd edn. Wiley, New York
- Sierra T (1996) Chapter 2. In: Serrano JL (ed) Metallomesogens. VCH, Weinheim
- Chohan ZH, Perrvez H, Kausar S et al (2002) Synthesis and characterization of antibacterial Co(II), Cu(II), Ni(II), and Zn(II) complexes of acylhydrazine derived pyrrolyl compounds. Synth React Inorg Met-Org Chem 32:529–543

- Takeshita TI, Wakebe A, Maeda S (1982) Synthesis of EDTA monoalkyl amide chelates and evaluation of the surface-active properties. J Am Oil Chem Soc 59:90
- Shuichi M, Kazayasu I, Sadao Y, Kazuo K, Tsuyoshi Y (1991) Surface activities, biodegradability and antimicrobial properties of n-alkyl glucosides, mannosides and galactosides. J Am Oil Chem Soc 67:996–1001
- Rosen MJ (1987) Surfactants and interfacial phenomena. Wiley, New York, p 72
- Aiad IA, Badawi AM, El-Sukkary MM, El-Sawy AA, Adawy AI (2012) Synthesis and biocidal activity of some naphthalene based cationic surfactants. J Surf Deterg 15:223–234
- 22. Gad EAM, El-Sukkary MMA, Ismail DA (1997) Surface and thermodynamic parameters of sodium *N*-acyl sarcosinate surfactant solutions. J Am Oil Chem Soc 74:43–47
- Przestalski S, Sarapuk J, Kleszcznska H, Habrielska J, Trela Z, Kuczera Z (2000) Influence of amphiphilic compounds on membranes. J Acta Biochem Polonica 47:627
- Badawi AM, Negm NA, El-Zahar SM (2004) Biocidal activity of some novel cationic metallomicelles. Met Ions Biol Med 8:89

Author Biographies

Ahmed I. Adawy is a researcher at the Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt. He was awarded his Ph.D. by Benha University, Egypt, for his study of surface and biological activity of some metallocationic surfactants. His research interests are in surfactants and their applications.

Mnal M. Khowdiary is a researcher at the Egyptian Petroleum Research Institute (EPRI), Cairo, Egypt. Her Ph.D. was awarded by Ain Shams University, Egypt, for her study of surface and biological activity of some metallocationic surfactants. Her research interests are in surfactants and their applications.